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Description

This invention relates to a process for recovering lead from copper refinery anode slime in order to upgrade the slime.

The presence of a large amount of lead in anode slime makes the recovery of precious metals and other valuable metals from the slime more difficult. A variety of techniques have been utilized to recover precious metals from the slime. None, however, has been commercially successful because of the large cost involved and the fact that it is difficult to recover precious metals from the slime. One type of technique involves direct smelting of slimes. This is disadvantageous as excessive formation of matte and slag causes heavy recirculation of precious metals. Such techniques involve roasting to convert copper to copper oxide followed by leaching of the roasted slimes with sulphuric acid. The leached slimes are then melted down in a small reverberatory (Doré) furnace in which the impurities are oxidized, leaving so-called Doré metal containing the precious metals, silver and gold. The Doré metal is then pasted to recover fine gold, fine silver, and any other previous metal present in the original slime. This particular technique is, as noted, disadvantageous because of the excessive formation of matte and slag.

A variety of other pyrometallurgical techniques combined with acid leaches and acid leach processes have also been attempted, but they are not suitable, mainly because it has not been possible to initially remove substantially all of the lead from the slime. It has not hitherto been found possible to remove the lead content of anode slime by acid leaching. The presence of lead in the slime has greatly inhibited the known processes from recovering precious metals from slime.

The present invention provides a process for upgrading anode slime containing lead and for recovering lead from the anode slime by leaching, in which leaching is carried out in a plurality of stages and the resulting solutions, together containing most of the lead content of the slime, are combined to form a solution from which lead acetate crystallizes.

In particular, the process comprises the following steps:

(a) subjecting the slime to primary leaching by means of a first ammonium acetate solution at a first temperature and for a first period of time such that the resulting first leach solution contains about 48% or more of the initial lead content of the slime;

(b) subjecting the residue from step (a) to secondary leaching by means of a second ammonium acetate solution at a second temperature and for a second period of time such that the resulting second leach solution and the first leach solution from step (a) together contain about 94% or more of the initial lead content of the slime;

(c) combining the first and second leach solutions resulting from step (a) and (b); and

(d) concentrating the combined solution so that lead acetate crystallizes out of the concentrated combined solution.

The solution resulting from step (b) preferably contains about 46% or more of the initial lead content of the slime. In other words, for optimum efficiency, the amount of lead extracted in the two steps is approximately equal, but the first step extracts slightly more than the second.

Preferably, the slime is leached with a solution of ammonium acetate at a temperature not exceeding 80°C. Thereby lead dissolution is maximized and dissolution of the other metals is minimized. The leach solutions used in the two steps are preferably substantially identical but may be different, depending on the practical circumstances.

The invention will be described further, by way of example, with reference to the accompanying drawing, whose sole Figure is a flow sheet of a process according to the invention.

The process can be utilized to upgrade any type of anode slime or mud produced in electrolytic refining of copper. The optimum processing parameters for any particular slime can be determined by making test runs based on the particular composition of such slime. Thus, for example, the leaching of a slime to remove lead, as discussed below, has need for a shorter period of time for those slimes containing low amounts of lead, and correspondingly a longer leach time for those slimes containing high amounts of lead.

Leaching may be effected under agitation in any conventional leaching vessel with an aqueous ammonium acetate solution with concentration greater than 0.1 mole dm⁻³, preferably from about 2 to 10 mole dm⁻³. The particular amounts of ammonium acetate used depend upon the concentration of lead in the slime being processed. For conventional slimes, amounts within the above range are adequate for an effective leach.

It is desirable to maintain a temperature of about 40°C throughout leaching and preferably not exceeding a temperature of about 60°C and the leaching steps are carried out for a total time sufficient to leach substantially all of the lead from the slime, to leave a lead content of preferably no more than about 3% based on the weight of the slime being leached. In general, this will take a total leach time of between 1 to 3 hours, again the particular time being dependent upon the slime treated. In general each leach will last at least 20 minutes, preferably 1 to 2 hours.

After leaching is completed, the leaching solution is separated from the undissolved slime. This can be accomplished by any conventional technique, preferably by filtration. The leach slurry can be thickened prior to filtration or filtered directly from the leach. The final solid

residue is dried and processed for shipment to plants for recovery of precious metals and other metal values. Because the lead has been removed, the dried processed anode slime is acceptable for treatment in recovery plants for selenium, tellurium, tin, silver, gold, and the like. The combined clarified or filtered solution is purified by the removal of the lead content by crystallization. The crystallized lead acetate from this purification step is recovered through filtration, decantation, or any solid-liquid separation techniques. The resultant clarified or filtered solution can be recycled back to the secondary leaching step for reuse, as shown in the drawing.

To more fully illustrate the determination of the optimum process parameters, the following examples are presented. It is to be understood, however, that these examples are given by way of illustration and not limitation.

Example I

A decopperized anode slime leaching experiment was carried out in a flask equipped with an agitator, a condenser, heating apparatus, and a temperature indicator and controller.

The sample of anode slime used possessed the following assay:

		wt %
5	Pb	26.6
	Ag	6.33
	Au	0.067
10	Cu	0.188
	Se	2.16
15	Sn	13.27
	moisture	3.2

845 gram (wet basis) samples of the slime together with the stoichiometric amount of ammonium acetate in various concentrations were placed in the said flask and heated for periods varying from 1 to 4 hours at a temperature of 40°C. The percentage of extraction of lead is set forth in Table I below.

TABLE I

CH ₃ COONH ₄ mole dm ⁻³	Leaching time, hours			
	1	2	3	4
	% Lead extracted			
2	17.62	19.11	19.95	20.19
3	25.04	26.00	25.67	27.53
4	33.07	34.82	36.17	37.50
5	43.86	44.95	45.13	45.98
6	49.93	52.10	51.09	50.25
7	51.14	51.07	52.27	52.36

Example II

Samples of decopperized anode slime having an assay similar to that set forth in Example I were leached in a manner similar to that set forth in Example I but at various temperatures

from 20 to 100°C. Ammonium acetate at a concentration of 6 mole dm⁻³ was used as the leaching reagent. The percentage of extraction of lead is set forth in Table II below.

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TABLE II

Leaching temp. °C	Leaching time, hours			
	1	2	3	4
	% Lead extracted			
20	41.71	42.50	42.79	43.00
40	48.67	51.60	50.57	50.01
55	37.25	38.87	36.95	36.50
75	34.75	35.60	33.67	33.17
100	27.68	26.82	25.63	25.00

Example III

Samples of decopperized anode slime having an assay similar to that set forth in Example I were leached twice with ammonium acetate solutions of various concentrations at 40°C. Each time a period of 2 hours was used for leaching. The overall percentage of extraction of lead is set forth in Table III below.

TABLE III

Ammonium acetate concentration mole dm ⁻³	% Lead extracted
2	34.74
3	48.31
4	67.39
5	79.20
6	95.23
7	93.13

Example IV

Samples of decopperized anode slime having an assay similar to that set forth in Example I were leached twice with 6 mole dm⁻³ ammonium acetate solution at various temperatures in the range from 20°C to 100°C. Each time a period of 2 hours was used for leach. The overall percentage of extraction of lead is set forth in Table IV below.

TABLE IV

Leach temp. °C	% Lead extracted
20	71.42
40	94.67
55	76.06
75	68.64
100	57.32

The pulp resulting from the optimum process (applied to 845 g of the slime) was filtered and the residue was dried and processed for shipment to plants for recovery of precious metals and other metals values. The analysis of the residue (424 g) was as follows:

	wt %
Pb	2.63
Ag	12.23
Au	0.13
Cu	0.326
Se	4.17
Sn	25.67
moisture	0.3

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The combined filtered solution at the leaching temperature of 40°C was analysed for metals, for which the results are set forth below:

Analysis of ammonium acetate leach solution (6525 ml)

Pb	mole dm ⁻³	0.1526
Ag	ppm	11.5
Cu	ppm	23.8
Se	ppm	<0.5
Sn	ppm	<4.0

The lead, silver, copper, selenium, and tin containing solution was heated until the total volume was reduced to one-third of the initial volume and then cooled down to below 40°C. Meanwhile, lead acetate crystallized out from the mother liquor. After filtration and drying, lead acetate with a purity of greater than 99.9% was obtained.

Claims

1. A process for upgrading copper refining anode slime containing lead and for recovering lead from the anode slime by leaching, characterised by the following steps:

(a) subjecting the slime to primary leaching by means of a first ammonium acetate solution at a first temperature and for a first period of time such that the resulting first leach solution contains about 48% or more of the initial lead content of the slime;

(b) subjecting the residue from step (a) to secondary leaching by means of a second ammonium acetate solution at a second temperature and for a second period of time such that the resulting second leach solution and the first leach solution from step (a) together contain about 94% or more of the initial lead content of the slime;

(c) combining the first and second leach solutions resulting from step (a) and (b); and

(d) concentrating the combined solution so that lead acetate crystallizes out of the concentrated combined solution.

2. A process as claimed in claim 1, in which the solution resulting from step (b) contains about 46% or more of the initial lead content of the slime.

3. A process as claimed in claim 1 or 2, in which the first or the second said temperature or each of them is in the range between 20 and 80°C.

4. A process as claimed in claim 3, in which the said temperature is about 40°C.

5. A process as claimed in any of claims 1 to 4, in which the first or the second ammonium acetate solution or each of them has an

ammonium acetate concentration greater than 0.2 mole dm⁻³.

6. A process as claimed in claim 5, in which the said concentration is about 6 mole dm⁻³.

7. A process as claimed in any of claims 1 to 6, in which the duration of the first or the second period or each of them is at least 20 minutes.

8. A process as claimed in claim 7, in which the said duration is 1 to 2 hours.

9. A process as claimed in any of claims 1 to 8, in which step (d) comprises heating the combined solution to above 40°C and subsequently cooling the combined solution to below 40°C.

Patentansprüche

1. Verfahren zum Aufarbeiten von Blei enthaltendem Kupferraffinierungs - Anodenschlamm und zur Wiedergewinnung von Blei aus dem Anodenschlamm durch Auslaugung, gekennzeichnet durch folgende Verfahrensschritte:

(a) der Schlamm wird einer primären Auslaugung durch eine erste Ammoniumacetat-Lösung bei einer ersten Temperatur und für eine erste Zeitdauer ausgesetzt, so daß die resultierende ersten Auslaugungslösung ungefähr 48% oder mehr des ursprünglichen Bleigehaltes des Schlammes enthält;

(b) der Rückstand von Schritt (a) wird einer sekundären Auslaugung durch eine zweite Ammoniumacetat-Lösung bei einer zweiten Temperatur und für eine zweite Zeitdauer ausgesetzt, so daß die resultierende zweite Auslaugungslösung und die erste Auslaugungslösung von Schritt (a) zusammen ungefähr 94% oder mehr des ursprünglichen Bleigehaltes des Schlammes enthalten;

(c) die aus den Schritten (a) und (b) resultierenden ersten und zweiten Auslaugungslösungen werden kombiniert; und

(d) die kombinierte Lösung wird konzentriert, so daß Bleiacetat aus der konzentrierten kombinierten Lösung auskristallisiert.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die aus dem Schritt (b) resultierende Lösung ungefähr 46% oder mehr des ursprünglichen Bleigehaltes des Schlammes enthält.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die erste oder die zweite Temperatur oder jede von ihnen im Bereich zwischen 20°C und 80°C liegen.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß die Temperatur ungefähr 40°C beträgt.

5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß die erste oder die zweite Ammoniumacetat-Lösung oder jede von ihnen eine Ammoniumacetat-Konzentration besitzt, die größer als 0,1 Mol dm⁻³ beträgt.

6. Verfahren nach Anspruch 5, dadurch ge-

kennzeichnet, daß die Konzentration ungefähr 6 Mol dm⁻³ beträgt.

7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß die Dauer der ersten oder der zweiten Zeitdauer oder jeder von ihnen mindestens 20 Minuten beträgt.

8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß die Zeitdauer 1 bis 2 Stunden ausmacht.

9. Verfahren nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß der Schritt (d) ein Aufheizen der kombinierten Lösung auf über 40°C und anschließendes Abkühlen der kombinierten Lösung auf einen Wert unterhalb von 40°C umfaßt.

Revendications

1. Procédé pour valoriser de la boue anodique de raffinage de cuivre, contenant du plomb, et pour extraire par lixiviation le plomb de la boue anodique, procédé caractérisé en ce qu'il comporte les étapes suivantes:

(a) à soumettre la boue à une première lixiviation à l'aide d'une première solution d'acétate d'ammonium à une première température et pendant une première période de temps, de manière que la première solution de lixiviation résultante contienne environ 48% ou davantage du plomb initialement contenu dans la boue;

(b) soumettre le résidu de l'étape (a) à une seconde lixiviation à l'aide d'une seconde solution d'acétate d'ammonium, à une seconde température et pendant une seconde période de temps, de manière que la solution résultant de la seconde lixiviation et la solution résultant de la première lixiviation de l'étape (a) contiennent ensemble environ 94% ou davantage du plomb initialement contenu dans la boue;

(c) combiner les solutions de première et de seconde lixiviation résultant des étapes (a) et (b); et

(d) concentrer la solution combinée de manière que l'acétate de plomb se sépare par cristallisation de la solution combinée et concentrée.

2. Procédé selon la revendication 1, dans lequel la solution résultant de l'étape (b) contient environ 46% ou davantage du plomb initialement contenu dans la boue.

3. Procédé selon l'une des revendications 1 ou 2, dans lequel la première ou la seconde température, ou chacune d'entre elles, se situe entre 20 et 80°C.

4. Procédé selon la revendication 3, dans lequel ladite température est d'environ 40°C.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel la première ou la seconde solution d'acétate d'ammonium, ou chacune d'entre elles, présente une concentration d'acétate d'ammonium supérieure à 0,1 mole dm⁻³.

6. Procédé selon la revendication 5, dans lequel ladite concentration est d'environ 6 moles dm⁻³.

7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel la durée de la première ou de la seconde période, ou de chacune d'entre elles, est d'au moins 20 minutes.

8. Procédé selon la revendication 7, dans lequel ladite durée est d'une à deux heures.

9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel l'étape (d) comprend le chauffage de la solution combinée jusqu'à une température supérieure à 40°C, puis le refroidissement de la solution combinée au-dessous de 40°C.

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